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(54) Title: METAL PIGMENT COMPOSITION

(57) Abstract

There is provided a process for preparing a low- or non-dusting substantially non-volatile (preferably highly light reflective) metal flake pigment composition, which comprises ball milling atomised metal powder in a milling fluid substantially comprised of water, in the presence of one or more corrosion inhibitors and a substance which acts as a lubricant for the milling process. Optionally, the paste may be formed into granules for easy storage. Preferred metal pigments are aluminium or gold bronze and in one embodiment the metal pigment is aluminum, the lubricant is oleic acid and the corrosion inhibitor is a phosphate ester having a polyethylene oxide side chain. Agent(s) having both lubricating and corrosion inhibiting properties are preferred as additives.

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1 **METAL PIGMENT COMPOSITION**

2

3 The present invention relates to a process for
4 preparing low- or non-dusting, substantially non-
5 volatile highly light reflective metal pigment
6 compositions by a ball milling process using water as
7 the major milling fluid.

8

9 The preparation of metal flake pigments is well
10 documented in the patent literature. For example, US
11 Patent 3901688 describes a wet ball milling process in
12 which metal powder or chopped foil is milled with an
13 organic liquid such as mineral spirits and a small
14 amount of a lubricant such as stearic or oleic acid.
15 The metal flakes so produced are separated, for example
16 by wet sieving to provide the desired particle size
17 distribution and thereafter brought to a paste-like
18 consistency of, typically, 55-80% weight metal content.
19 In this conventional process the lubricant is required
20 to avoid cold welding of the metal flakes under the
21 action of the grinding media. The purpose of the
22 organic liquid is to reduce the viscosity of the
23 system, enabling efficient conversion of the starting
24 powder to flakes.

25

1 Metal flakes may also be prepared in the complete
2 absence of solvent by a dry ball milling process, such
3 as that described in US Patent 4115107.

4

5 A further method of preparation of metal flake is by
6 electrodeposition of a thin film of metal onto an inert
7 support, followed by removal and fragmentation into
8 flakes. The product is generally provided either as
9 dry flake or as a dispersion of the metal flakes in
10 solvent.

11

12 The aforementioned methods for preparing metal flake
13 pigments suffer from a number of disadvantages. For
14 example, dry milling processes are now little used, due
15 to the explosive and contaminating properties of the
16 dry flake products. Though the paste form, in which
17 the metal flake particles are damped by solvent, is
18 inherently safer and easier to handle, it is not
19 without problems. The 20-45% by weight solvent portion
20 of metal pigment pastes may be acceptable in certain
21 coating applications such as automotive paints, but in
22 others, especially printing inks, such solvents
23 typically slow down the drying rate and may cause odour
24 in the final printed film, due to retention of minute
25 concentrations of these typically high boiling point
26 solvents. This is especially disadvantageous in
27 printed films on packaging intended for food contact.
28 The presence of organic solvent in other application
29 areas, such as plastics, can also be very undesirable.
30 The solvent vaporises during processing, causing
31 bubbles and surface blemishes in the pigmented plastic
32 article.

33

34 Flake formation by the electrodeposition process can
35 give very bright flakes of narrow particle size
36 distribution, but it is a very costly process, unsuited

1 to large scale production. This is because the
2 equipment required to maintain the hight vacuum
3 environment in which the metal is vaporised is very
4 expensive to construct and operate.

5

6 It is also found that the storage stability of the
7 metal pigment pastes themselves is finite, due to the
8 tendency of the organic solvent component to evaporate,
9 leading to aggregation of the metal flake particles.
10 This is especially true for pastes in which a more
11 highly volatile solvent has been employed, perhaps to
12 ensure the compatibility of the metal pigment paste in
13 a particular coating system. Once aggregated,
14 redispersion is difficult. In derived coatings, hiding
15 power, or opacity, and also gloss, may be greatly
16 reduced.

17

18 Increasingly too, environmental concern about organic
19 solvent is leading to legislation which encourages a
20 lower use of volatile solvents in industrial processes.
21 The costs associated with solvent purchase, storage and
22 recovery are increasing. Containment equipment,
23 required to meet increasingly severe legislative
24 constraints on the emission of solvent to the
25 atmosphere is expensive. As a result replacement of
26 organic solvents by water is a strategic goal in many
27 industries.

28

29 Recent changes in health and safety classifications
30 require a number of high boiling point petroleum
31 derived hydrocarbon solvents traditionally used in
32 metal pigment manufacture to be designated
33 carcinogenic. This increases the pressure for their
34 elimination from metal flake pigment manufacturing
35 processes.

36

1 The need for a stable, safe and easily handled product
2 metal pigment form, free of the disadvantages of both
3 dry flakes and solvent containing pastes has been met
4 by the products of European Patent 0134676. There is
5 described therein a process for the preparation of a
6 solid low- or non-dusting, metal pigment composition
7 which comprises forming a coherent paste of an organic
8 binder medium, an organic liquid vehicle and metal
9 pigment, in powder or flake form, the paste being
10 formed by mixing a first component comprising organic
11 binder medium and a second component comprising metal
12 pigment, with either or both of the first and second
13 components comprising organic liquid vehicle and the
14 paste containing from 3-45% of the organic binder
15 medium based on the weight of the metal pigment, and
16 either sub-dividing the coherent paste into particles
17 and removing substantially all organic liquid vehicle
18 from the particles, or removing substantially all the
19 organic liquid vehicle from the coherent paste and sub-
20 dividing the resulting mass into particles, at least 98%
21 by weight of the resulting particles being retained on
22 a sieve having a 150 µm aperture and each containing a
23 plurality of metal pigment particles dispersed in a
24 matrix of organic binder medium. The so-called
25 "granule" products of this process can be prepared
26 using organic binder media compatible with the end
27 application. Thus, for example, synthetic aldehyde and
28 ketone resins could be employed for ink applications
29 and polyolefin derivatives for the mass pigmentation of
30 thermoplastics.

31

32 Though the products of European Patent 0134676 are
33 substantially free of organic solvent, the process
34 itself still involves processing of solvent. It is
35 thus still subject to the aforementioned legislative
36 pressures. There is therefore a clear need for a

1 process for preparing an easily handled, dust free,
2 metal pigment product, which does not employ organic
3 solvents.

4

5 It is possible to prepare a dust free, metal pigment
6 product without the use of organic solvents if the
7 metal pigment is prepared by dry milling and thereafter
8 incorporated into a suitable organic carrier material
9 by mixing at a temperature above the melting point of
10 the organic carrier. Once a homogeneous mixture has
11 been attained, the mass is cooled, often with extrusion
12 into a more easily handled form, such as granules or
13 pellets. Such processes were once widely employed for
14 the preparation of plastics masterbatch. The need to
15 use dry metal pigments, with their attendant
16 disadvantages, and the difficulty of wetting such
17 pigments satisfactorily into the carrier resin, have
18 contributed to the decline in this type of process.
19 Although the problem of metal flake dusting may be
20 reduced if the metal powder precursor is milled in the
21 presence of the carrier resin, methods traditionally
22 used to separate wanted from unwanted particle size
23 fraction, such as dilution with solvent and screening,
24 are then no longer operable.

25

26 A more satisfactory processing liquid is water. It is
27 readily available, inexpensive and non-flammable.
28 However, a difficulty arises in the case of the more
29 reactive metal pigments, especially aluminium, which is
30 the most widely used of such pigments. Aluminium metal
31 may react with water to form aluminium oxide and
32 hydrogen gas, according to the equation:-

33



35

36 Generation of hydrogen is dangerous, because it is

1 highly explosive. Sealed containers of aqueous metal
2 pigment pastes may become pressurised and explode. In
3 addition, the pigmentary properties of the metal flake
4 are destroyed.

5

6 Many attempts have been made to stabilise aluminium
7 against this reaction. Methods employed fall into
8 several categories, for example resin encapsulation or
9 chemical treatment. As an example of the former, there
10 may be mentioned United States Patent 4213886.

11 Prominent types of chemical treatment are silica
12 coating (see, for example, United States Patent
13 2885366), treatment with chromium derivatives (German
14 Patent 3636183), phosphate treatment, described in
15 European Patent 0319971 and vanadium treatment
16 (European Patent 0104075).

17

18 Milling aluminium powder in a mixture of water and an
19 organic solvent has been described in United States
20 Patent 3565655. Morpholine is used as a corrosion
21 inhibitor with a fatty acid as the milling lubricant.
22 However, the presence of at least 2 weight percent of a
23 hydrocarbon or a halogenated hydrocarbon is a necessary
24 part of the invention.

25

26 United States Patent 4693754 describes the milling of
27 aluminium powder in a mixture of hydrocarbons, water,
28 and a compound of chromium or vanadium which acts as a
29 corrosion inhibitor. However again the presence of
30 some organic solvent in the milling process is a
31 component part of the invention.

32

33 In WO-A-94/28074 there is described for the avoidance
34 of odour the milling of aluminium powder, optionally
35 with solvent or water, without a fatty acid lubricant,
36 but in the presence of a polymer resin that is a paint

1 or ink binder. This Patent Application does not
2 include the use of a corrosion inhibitor in the milling
3 process. In the absence of a corrosion inhibitor,
4 water milled aluminium pigments are prone to severe
5 gassing and result in products having a dull grey
6 colour, in contrast to the bright metallic effects
7 desired for decorative metallic finishes.

8

9 There is, therefore, still a need for a satisfactory
10 process which can be used for milling aluminium powder
11 and the like without organic solvent.

12

13 According to the present invention, there is provided a
14 process for preparing a low- or non-dusting,
15 substantially non-volatile (preferably highly light
16 reflective) metal flake pigment composition, which
17 comprises ball milling atomised metal powder in a
18 milling fluid substantially comprised of water, in the
19 presence of one or more corrosion inhibitors and a
20 substance which acts as a lubricant for the milling
21 process.

22

23 Thereafter, unwanted oversize or undersize particles
24 may be removed. In the next stage of the process the
25 aqueous metal pigment slurry may be used unaltered, may
26 be converted to a dry metal flake pigment powder by
27 removal of the milling fluid, for example at elevated
28 temperature, or is preferably concentrated to a paste-
29 like consistency. The metal flake pigment can be
30 incorporated in an organic binder medium by mixing to
31 form a coherent paste of an organic binder medium,
32 water and metal flake pigment, the paste being formed
33 by mixing a first component comprising organic binder
34 medium and a second component comprising metal pigment,
35 with either or both of the first and second components
36 comprising water and the paste containing from 1 to

1 150%, preferably 3-70%, and most preferably 30 to 60%
2 of the organic binder medium based on the weight of the
3 metal pigment, and either sub-dividing the coherent
4 paste into particles and removing substantially all
5 volatile liquids from the particles, or removing
6 substantially all the volatile liquids from the
7 coherent paste and sub-dividing the resulting mass into
8 particles, at least 98% by weight of the resulting
9 particles being retained on a sieve having 150 μm
10 aperture and each containing a plurality of metal
11 pigment particles dispersed in a matrix of organic
12 binder medium, the organic binder medium being capable
13 of binding the metal flake pigment particles by either
14 precipitation from solution during volatile liquid
15 removal, or melting or sintering at elevated
16 temperature and fusion.

17

18 The volatile liquid will usually consist substantially
19 of water. For example, the volatile liquid may be
20 water together with small amounts of additives, for
21 example lower alcohols as wetting agents and resin
22 solubilisers and dispersers.

23

24 The milling fluid used in the present invention
25 consists substantially of water. The presence of up to
26 50% by volume (for example up to 30%, especially up to
27 25%, more especially up to 10%) of an organic solvent
28 can usually be tolerated. A small amount (for example
29 less than 2%) of an organic solvent is generally
30 acceptable. Lower alcohols are especially useful as
31 defoaming agents. Any such organic solvent is
32 desirably water miscible. In one embodiment the
33 milling fluid consists only of water and the system
34 contains no organic liquid at all, the only organic
35 compounds present being additives such as the
36 lubricant(s), corrosion inhibitor(s) etc.

1 One of the advantages of the process of the present
2 invention is the possibility of treating the milled
3 flakes whilst in an aqueous system. For example, the
4 milled flakes can be chromate treated or coated with
5 silica or alumina prior to any granule formation. Such
6 a process enables the pigments to be rendered suitable
7 for different applications or to have different colour
8 characteristics. Such aqueous treatments are known in
9 the art, but tend to be difficult and expensive to
10 carry out since the traditional milling fluid must be
11 removed before the pigments can be treated in an
12 aqueous medium. Since the milling process of the
13 present invention is carried out in water, such
14 treatments are simple to conduct.

15

16 The substantially aqueously carried product of the
17 milling step could be added to surface coating binders
18 dissolved or dispersed in water, solvent or mixtures of
19 the two, to prepare a surface coating, such as an ink
20 or paint. The reaction of certain metal flake
21 pigments, notably aluminium, is, however unpredictable.
22 As such a surface coating contains a proportion of
23 water there exists the possibility that reactions may
24 occur during storage, with the formation of hydrogen
25 gas and associated hazards.

26

27 It is a further advantage of the process of the
28 invention that water is substantially eliminated from
29 contact and potential reaction with the metal pigment
30 through the formation of the substantially non-volatile
31 metal pigment composition.

32

33 Metals suitable for the performance of the invention
34 include all those metals commercially employed as flake
35 pigments, such as aluminium, zinc, copper, tin, nickel,
36 iron and alloys thereof, such as gold bronze (an alloy

1 of copper and zinc) or stainless steel (an alloy
2 composed mainly of iron, nickel and chromium).
3 Aluminium and gold bronze are preferred. There is no
4 criticality to the particle size of the milled flakes,
5 but a flake diameter range of 6 µm to 600 µm,
6 preferably 10 µm to 300 µm is generally suitable.
7 Advantageously, the particles produced are well
8 flattened highly light reflective flake pigments.
9

10 Any compounds capable of inhibiting the reaction of the
11 metal with water may be employed as corrosion
12 inhibitors, for example phosphorus-, chromium-,
13 vanadium- or silicon-containing compounds. They may be
14 used individually or in admixture.

15
16 Suitable phosphorus compounds may be organic or
17 inorganic. Simple inorganic phosphates, such as
18 calcium or magnesium phosphate, or more complex
19 phosphosilicate compounds may be used. The latter
20 include calcium phosphosilicate, calcium strontium
21 phosphosilicate and aluminium zirconium zinc
22 phosphosilicate. An especially preferred member of
23 this class is calcium strontium zinc phosphosilicate.
24

25 Organic phosphorus compounds include alkyl and dialkyl
26 phosphates and phosphites, with the alkyl groups
27 containing 2-20 carbon atoms. Iso-octyl acid phosphate
28 may be particularly mentioned. Also suitable are
29 phosphate esters of long chain ethoxylated alcohols.
30 Preferred amongst these is Briphos S2D, a product of
31 the Albright & Wilson company, which is an ethoxylated
32 phosphate ester.
33

34 Silicon containing compounds capable of inhibiting the
35 reaction of metals with water include organic silanes
36 and silicates, especially tetraethyl silicate, and

1 inorganic silicon compounds such as potassium silicate.

2

3 Salts of molybdenum, vanadium and tungsten, especially
4 the ammonium salts, have also shown particular
5 suitability in the process of the invention.

6

7 Chromium compounds suitable for the process of the
8 invention include ammonium dichromate and chromic acid.
9 In this class, the former is preferred as it is less
10 aggressive towards metal grinding media.

11

12 Amongst the above corrosion inhibiting compounds, non-
13 resinous organic or inorganic phosphates are especially
14 preferred. They generally offer a high level of metal
15 passivation with few health and safety concerns.

16

17 Lubricants suitable for the process of the invention
18 are generally organic compounds recognised in the art
19 as having surfactant properties. Non-ionic
20 surfactants, such as ethylene oxide condensates with
21 aliphatic alcohols or phenols are effective without
22 affecting the pH of the system. In general it is
23 desirable that the pH is kept as close to neutral as
24 possible to assist in the prevention of corrosive
25 attack of the metal surface. Such lubricants may also
26 be advantageous in the metal segregation and recovery
27 stages of the process, for example to overcome the
28 surface tension of water to ensure efficient screening.
29 Surprisingly, fatty acids, such as oleic and stearic
30 acids, widely used as lubricants in the solvent based
31 ball milling of metal powders, are also effective in
32 the milling step, especially when made active in the
33 aqueous phase by surfactants or by formation of a water
34 soluble alkali salt. In the same way, water insoluble
35 plasticisers may be used, for example phthalates such
36 as dioctyl or diisodecyl phthalate, and adipates, such

1 as dioctyl adipate.

2

3 Also suitable as lubricants are polyethylene oxides and
4 glycols and polypropylene oxides and glycols of various
5 molecular weights. Those displaying some water
6 solubility are preferred.

7

8 It may also be desirable to add small quantities of
9 organic compounds recognised in the art for their
10 defoaming properties. For example, acetylenic diols
11 may be used, but the inexpensive lower alcohols are
12 also effective.

13

14 Advantageously, surfactants may be employed. Examples
15 include anionic, non-ionic and cationic surfactants,
16 including the solid alkyl ether phosphates such as the
17 "Crodafos CS" (Registered Trade Mark) range of Croda
18 Chemicals Ltd, alkylaryl sulphonates and their alkali
19 metal derivatives such as alkali toluene sulphonates,
20 alkali xylene sulphonates, alkali naphthalene
21 sulphonates, alkali diisopropyl naphthalene sulphonates
22 and alkali dodecyl benzene sulphonates; alcohol
23 sulphates such has sodium lauryl alcohol sulphate,
24 sulphosuccinates such as sodium dioctyl
25 sulphosuccinate, sarcosinates such as lauroyl sarcosine
26 and stearyl sarcosine; fatty amines such as
27 stearylamine, and distearylamine; amine salts such as
28 coconut fatty amine acetate; alkyl phenol ethoxylates
29 such as nonyl phenol ethoxylate; alcohol ethoxylates
30 such as higher ethoxylated oleyl alcohol; higher
31 polyoxypropylene-polyoxy ethylene copolymers, such as
32 alkylolamides such as myristic diethanolamide and
33 coconut mono-isopropanolamide, esters such as propylene
34 glycol monostearate and cetyl palmitate; maleic
35 anhydride copolymers such as the disodium salt of
36 maleic anhydride and di-isobutylene, and the SMA series

1 of low molecular weight styrene-maleic anhydride
2 copolymers.

3

4 Phosphate esters (eg Biophos S2D) which also have
5 lubricating and/or corrosion inhibiting properties are
6 preferred.

7

8 In a preferred embodiment, additive(s) having corrosion
9 inhibiting, surface tension reducing and lubricating
10 properties are present in the milling step.

11

12 Milling lubricants prevent cold welding of flakes which
13 typically takes place during the ball milling process.
14 The corrosion inhibitor and milling lubricant functions
15 may be provided by a single chemical substance, for
16 example a substituted phosphate ester (such as Briphos
17 S2D), or the functions may be provided by two or more
18 different materials.

19

20 There is no criticality to the mechanism of
21 commminution. Any comminution process known in the art
22 for metal flake production may be employed, providing
23 the mechanical energy imparted is not so severe as to
24 damage the metal flakes being formed. Ball milling is
25 a widely operated process.

26

27 Neither is there any criticality to the grinding media,
28 providing they do not react chemically with the other
29 components during or after the comminution stage of the
30 process. Stainless steel and high density ceramic
31 grinding media are generally satisfactory.

32

33 Unwanted oversize or undersize metal flake particles
34 are removed by any suitable means, such as screening of
35 a slurry diluted by more water. The aqueous metal
36 pigment slurry can then be concentrated to a paste by

1 an convenient means, such as a filter press, ready for
2 admixture with the organic binder medium.

3

4 Organic binder media include those organic materials
5 habitually employed as binders in paints and inks or as
6 plastics masterbatch carriers. The organic binder
7 chosen is dependent on the envisaged end use of the
8 product of the invention. Thus, if desired, the binder
9 can be a solvent-soluble resin. As examples of organic
10 binder media there may be mentioned cellulose acetate
11 butyrate (CAB) and cellulose acetate propionate (CAP)
12 resins, coumarone indene, epoxy esters, epoxide
13 melamine and epoxide phenolic condensates, ketone,
14 aldehyde, maleic and phenolic resins and also rosin,
15 cellulose and petroleum derived resins, together with
16 thermoplastic polymers, such as polyacrylates,
17 polyolefins, polyvinyls, styrenics, polyamides,
18 polyesters and copolymers thereof. Also suitable are
19 natural and synthetic waxes, such as montan and
20 paraffin wax and synthetic waxes such as polyethylene
21 and polypropylene waxes. Where it is desired to
22 introduce liquid organic binders, such as plasticisers,
23 for example to improve application properties, they are
24 desirably added in minor proportions in combination
25 with solid resins, to provide structural rigidity in
26 the resulting metal pigment particles. Such
27 plasticisers include mineral oils as well as phthalates
28 such as dioctyl or diisodecyl phthalate, and adipates
29 such as dioctyl adipate.

30

31 Gelatin and carrageenen are useful water soluble
32 organic binders due to their suitability for food
33 contact applications.

34

35 In a preferred embodiment the binder material is a non-
36 resinous material.

1 The products of the invention are typically in a form,
2 such as tablet, pellet, granule, flake or spherical
3 bead, which provides the attributes of ease of
4 handling, low- or non-dusting and meterability.
5 Granules having a length of 5-20mm, a cylindrical cross
6 section and a diameter of 1.5-3mm are preferred, as
7 they have been found to offer optimum handling
8 characteristics, especially in plastics applications
9 where it is important to prevent stratification of
10 polymer pellets and the particularly dense products of
11 the invention. Apparatus used for the preparation of
12 such physical forms is well known to those skilled in
13 the art and is described in, for example, European
14 Patent 0134676.

15

16 The function of the organic binder medium is to bind
17 the metal pigment flakes together to prevent them
18 becoming airborne as dust. Where the organic binder
19 medium is soluble or dispersible in water, it may be
20 added as an aqueous solution or dispersion. Where it
21 is insoluble in water it is preferable to micronise the
22 binder. In this latter case, the coherent paste of
23 metal pigment, water and micronised organic binder
24 medium is formed into particles, for example by mixing
25 and extrusion, then dried at for example 60°C to remove
26 substantially all the water, then heat treated at
27 elevated temperature, for example 100 to 130°C for a
28 short time, to fuse together the micronised organic
29 binder medium and the metal pigment. This process is
30 particularly suited to products for the plastics
31 market, in which suitable organic binder media tend to
32 be insoluble in water. It provides a final product
33 form which has excellent colouristic and application
34 properties when used in the injection moulding or
35 extrusion of thermoplastics.

36

1 In extreme cases the chosen binder may be insoluble in
2 water and unsuitable for micronising and fusion. In
3 such cases the binder may be dissolved or dispersed in
4 a suitable organic solvent prior to admixture with the
5 metal pigment component. Such a solvent is desirably,
6 though not essentially, water miscible.

7

8 In a preferred embodiment the metal is aluminium.
9 Conveniently the lubricant is a mixture of a surfactant
10 and a fatty acid, such as oleic or stearic acid. Oleic
11 acid in an amount of 1 to 100%, preferably 2 to 60%,
12 most preferably 3 to 8%, for example approximately 5%,
13 by weight relative to the metal has been found to be
14 effective in mixture with non-ionic surfactants at 5-
15 15%. The corrosion inhibitor may advantageously be a
16 phosphate ester having a polyethylene oxide side chain.

17

18 The invention is further illustrated by the following
19 Examples in which all parts and percentages are by
20 weight, unless otherwise stated.

21

22 Example 1

23

24 To a cylindrical mill of diameter 21 cm were added:
25 5000g of 1/8 inch (3.2mm) diameter stainless steel
26 balls;
27 500g of distilled water;
28 100g of fine particle size, aluminium powder; and
29 13g of Briphos S2D, which had been pre-neutralised with
30 triethanolamine - this makes the Briphos more soluble
31 and reduces attack of the aluminium. Briphos S2D is a
32 phosphated ester of a long chain ethoxylated alcohol
33 manufactured by Albright and Wilson. The mill was
34 rotated at 80 rpm for 4 hours and the aluminium pigment
35 so formed separated from the steel balls by sieving,
36 prior to recovery in a filter funnel.

1 In a laboratory mixer, a quantity of the aluminium
2 flake pigment thus obtained, containing 25.0g solids,
3 was added to 10.7g Hoechst Ceridust 3620, a micronised
4 polyolefin wax with a particle size of less than 22
5 microns. The mixture was formed into granules by
6 extrusion through a 2mm diameter die, and dried in an
7 oven held at a temperature of 60°C +/- 10°C for two
8 hours. The granules were then placed in an oven held
9 at 115°C +/- 10°C for 10 minutes to fuse the organic
10 binder medium. 35.1g of substantially water free, non-
11 dusting, free flowing, meterable granules of approx.
12 12mm length and of good abrasion resistance were
13 obtained.

14
15 A test piece made by injection moulding the granule in
16 polystyrene at a level of 1% calculated on polymer
17 weight, had a smooth, fine and bright silvery
18 appearance.

19
20 **Example 2**

21
22 The following mixture was milled in a cylindrical mill
23 as described in Example 1, with the following
24 formulation:-
25 5000g of 1/8 inch (3.2mm) diameter stainless steel
26 balls;
27 500g of distilled water;
28 100g of aluminium powder of approx. 33µm average
29 particle diameter;
30 13g of Briphos S2D, which had been neutralized with
31 triethanolamine;
32 2.85g of Antarox V27, a linear C₈₋₁₀ aliphatic alcohol;
33 ethoxylate/propoxylate alcohol manufactured by Rhone-
34 Poulenc Chemicals; and
35 0.15g of Surfynol 104, an acetylinic diol from Air
36 Products.

1 A quantity of the derived aluminium flake pigment
2 paste, containing 24.1g solids, was added to 10.3g of
3 FE 532-00, a micronised ethylene vinyl acetate resin
4 sold by Croxton and Garry. The mixture was granulated,
5 dried and heat treated as in Example 1. A test piece
6 made by injection moulding the granule in polypropylene
7 at a level of 3%, calculated on polymer weight, had a
8 bright, highly sparkling, silvery appearance.

9

10 **Example 3**

11

12 The method of Example 1 was repeated with the
13 substitution of Hoechst Ceridust 3620 by an equal
14 weight of Polyox WSR 301, a solid, non-ionic, high
15 molecular weight, water-soluble, polyethylene oxide
16 polymer. The mixture was formed into granules by
17 extrusion through a 2mm diameter die, and dried in an
18 oven held at a temperature of 50°C +/- 10°C for four
19 hours. 35.2g of substantially water free, non-dusting,
20 free flowing, meterable granules of approx. 12mm length
21 and of good abrasion resistance were obtained.

22

23 An aqueous printing ink was prepared by combining the
24 following:-

25 20g of the granule product of this Example, dispersed
26 in 25g water and let down with
27 53g Zinpol 132, an acrylic resin emulsion of 40%
28 solids, supplied by Worlee Chemie and
29 2g waxes and defoaming additives.

30 The ink thus formed was stable to gassing and provided
31 a smooth, bright metallic silver effect when printed on
32 a paper substrate.

33

34 **Example 4**

35

36 10g Halox ZSP 391, a calcium strontium zinc phospho-

1 silicate compound, sold by Halox Pigments of Hammond,
2 Indiana, United States of America.
3 3g oleic acid,
4 5g Pluriol 600, a polypropylene glycol supplied by BASF
5 A.G., and
6 50g deionised water
7 were high speed stirred to solution.
8 35.1g of solution,
9 219.4g deionised water, and
10 30g atomised aluminium powder of approx. 8µm average
11 particle diameter
12 were set on a vibratory mill with 1500g 1/8 inch
13 (3.2mm) diameter stainless steel balls, in a rigid
14 plastic pot. After 4 hours, the contents were removed
15 and separated from the steel balls. Water was added to
16 a metal concentration of about 3% and the slurry
17 screened on a 400 mesh screen. The undersize fraction
18 was concentrated in a filter press to about 80% metal
19 content, then combined with Microthene 532-00, an
20 ethylene vinyl acetate polymer sold by Croxton & Garry
21 Ltd, by the fusion process of Example 1.

22
23 When injection moulded at 1.5% w/w in polypropylene,
24 the granule exhibited a particularly bright, reflective
25 silver coloration, with good dispersion.

26
27 The dispersibility characteristics of this product can
28 be further enhanced by replacing up to 30% of the
29 Microthene by a high boiling mineral oil such as
30 Kaydol, manufactured by Witco.

31
32 Example 5

33
34 200g Halox SZP-391
35 100g Pluriol P600
36 100g Antarox V27

1 100g water and
2 60g oleic acid
3 were high speed stirred for 10 minutes to form a
4 homogeneous mixture. To a cylindrical mill of diameter
5 21cm were added: 5000g of 1/8 inch (3.2mm) diameter
6 stainless steel balls, 75g of the above mixture, 100g
7 aluminium powder of 9 μm median particle diameter and
8 375g of distilled water.

9
10 The mill was rotated at 105 rpm for 6 hrs to form a
11 flake pigment product of approximately 25 μm median
12 particle diameter. The grinding media were removed on
13 a coarse screen and the product itself screened on a
14 400 mesh (38 μm) screen using water as the washing
15 liquid. The flake passing through the screen was
16 concentrated on a filter funnel. When converted to a
17 granule and tested in the water based ink system of
18 Example 3, this material provided a bright silver
19 effect with good coverage and good adhesion to a paper
20 substrate.

21
22 The Halox SZP-391 of this Example may be replaced by
23 members of the Heucophos range of multiple metal
24 phosphates manufactured by Heubach GmbH, with similar
25 results.

26

27 **Example 6**

28

29 19g AntaroZ V27 and
30 1g Surfynol 104
31 were warmed and mixed together to form a homogeneous
32 liquid, which was mixed into 120g of the water based
33 paste intermediate of Example 1, containing 80g metal,
34 to form a stiff paste. The paste was extruded through
35 a 2.5mm diameter die into strands and the water removed
36 by drying at 70°C. The resulting dry strands were

1 broken up into granules of approximately 1cm length.
2 An aqueous ink was prepared by predispersing the
3 granules in a small quantity of water into which the
4 Zinpol medium of Example 3 was thereafter blended. A
5 bright ink, with good stability and coverage was
6 obtained.

7

8 The Antarox and Surfynol in this example may be
9 replaced by 20g of the natural product carageenen in
10 powder form with similar results. Such a granule has
11 particularly good shelf life and redispersion in water.

12

13 **Example 7**

14

15 To a 0.5 litre capacity vibratory pot mill were added:-

16

17 1.5kg of 2.4mm diameter ceramic grinding media,
18 150g water,
19 30g aluminium powder of 7 μ m average particle diameter,
20 2.5g iso-octyl acid phosphate and sufficient 25%
21 aqueous ammonia to maintain the pH at approximately 7.

22

23 The charge was milled for 3 hrs then recovered,
24 screened, formed into granules and tested as in
25 Example 5. The printed ink had similar brightness, but
26 superior coverage to that of Example 5.

27

28 **Example 8**

29

30 To 0.5 litre capacity vibratory pot mill were added:-

31

32 1.5kg of 3mm diameter stainless steel grinding media,
33 150g water,
34 30g aluminium powder of 7 μ m average particle diameter,
35 2.4g Briphos S2D and . . .
36 0.6g 25% aqueous ammonia.

1 The charge was milled for 4 hrs, then discharged with
2 water and screened on a 400 mesh ($38\mu\text{m}$) screen. The
3 fraction passing through the screen was collected and
4 concentrated under vacuum in a filter funnel. A
5 quantity of the filter cake, corresponding to 80g metal
6 was thoroughly mixed with 20g of a commercial source of
7 C₁₂₋₁₄-aliphatic alcohols. The stiff paste was formed
8 into pellets and the water removed at 65°C. The
9 resulting product had good stability and colouristic
10 properties in a one pack UV curing resin system.

11

12 **Example 9**

13

14 The milled, screened and recovered paste product of
15 Example 8 was mixed with micronised Laropal K80 ketone
16 resin, manufactured by BASF AG in the ratio 80 parts by
17 weight of metal to 20 parts by weight of resin. The
18 mixture was formed into granules by extrusion and the
19 water removed in an oven of 70°C.

20

21 When tested in a solvent based ink, the granular
22 product displayed similar characteristics to a granule
23 prepared by the methods described in EP-A-0134676 using
24 a conventional solvent milled paste as starting
25 material.

26

27 **Example 10**

28

29 An amount of the milled, screen and recovered paste
30 product of Example 8 corresponding to 80g metal was
31 placed in a 1 litre beaker fitted with a propeller
32 agitator set at 400 rpm. With agitation there were
33 then added,
34 530g Dowanol PB29, an ether-alcohol solvent of the Dow
35 Chemical Co,
36 26.7g of 25 % aqueous ammonia,

1 20g tetraethyl silicate and finally another
2 26.7g of 25% aqueous ammonia.
3 The mixture was agitated for 5 minutes, then there was
4 added another 26.7g of 25% aqueous ammonia.

5

6 After a further two hours mixing, air was bubbled
7 through the slurry for 2 hours to remove excess ammonia
8 and the metal recovered on a Buchner filter.

9 Thereafter, the filter cake was converted to a gold
10 pigment by the process of Example 1 of our co-pending
11 British Patent Application No 9609507.0 (ie was stirred
12 at 600 rpm with a paddle agitator for one hour, then
13 filtered under vacuum on a Buchner funnel, and washed
14 with excess water. The product was a viscous paste
15 dispersible in both water and oxygen-containing
16 hydrocarbon solvents) and then to a granule by the
17 process of Example 25 of EP-A-0134676. The granules so
18 formed provided a rich gold coloration in water based
19 paints and inks.

20

21 **Example 11**

22

23 2g of oleic and
24 2g of Antarox V27 and Surfynol 104 in 19:1 weight ratio
25 were mixed together and added dropwise to
26 140g vigorously stirred water in a beaker containing
27 1g isopropanol, to form an emulsion. There was then
28 added

29 4g hydrogen peroxide (30%w/w; 100 volume) and the whole
30 added to

31 30g A 7401 atomised aluminium powder of 8 μ m average
32 particle diameter in a ball milling pot of 500ml volume
33 containing

34 1500g spherical, stainless steel grinding media of 3mm
35 average diameter.

36 The pot was sealed and placed on a vibratory mill for

1 4 hours. The charge was washed out with
2 200g water, screened on a 400 mesh screen and an
3 aqueous paste recovered by vacuum filtration.
4 The water was removed by drying at 50°C and 16g of the
5 resulting fine flake powder incorporated into
6 8.89g Worleesol 31, a modified linseed oil polymer
7 (supplied by Worlee Chemie as a 45% solution in 80/20
8 w/w water/2-butoxy ethanol), further diluted in
9 3.5g of a 60/40 weight ratio mixture of water and
10 isopropanol.

11 After forming into granules and evaporating the
12 volatiles at 60°C, the soft, dry product was found to
13 give a bright, high coverage silver finish in an
14 exclusively isopropanol based or water/isopropanol
15 based varnish.

16

17 **Example 12**

18

19 A formulation comprising
20 1500 spherical, ceramic grinding media of 3mm average
21 diameter,
22 150g water,
23 30g aluminium powder of 8µm average particle diameter,
24 2.4g Crodrafos 25D5A, an ethoxy (5) C₁₂₋₁₅ alcohol acid
25 phosphate ester, supplied by Croda Ltd and
26 0.6g ammonia, 25% in water was loaded into a 500ml pot
27 and milled on a vibratory mill for 3 hours.

28 The grinding media was removed on a coarse screen and
29 the metal flake pigment product screened on a 400 mesh
30 (38µm) screen using water as the washing liquid. The
31 flake passing through the screen was concentrated on a
32 filter funnel. When converted to a granule with a
33 carageenan carrier and tested in the water based ink
34 system of Example 3, this material provided a bright
35 silver effect with good coverage.

36

1 **Example 13**

2

3 The method of Example 12 was repeated with the
4 substitution of Crodrafos 25D5A by an equal weight of
5 Crodrafos T5A, an ethoxy (5) isotridecanol acid
6 phosphate ester. Similar results were obtained on
7 conversion to a granule and testing as described
8 therein.

9

10 **Example 14**

11

12 The method of Example 12 was repeated with the
13 substitution of Crodrafos 25D5A by an equal weight of
14 Crodrafos N10N, an ethoxy (10) oleyl alcohol phosphate
15 ester diethylamine salt. Similar colouristic results
16 were obtained on conversion to a granule and testing as
17 described therein. This material, however, also had
18 outstanding adhesion to the paper substrate, as
19 demonstrated by a tape test.

20

21 **Example 15**

22

23 A formulation comprising
24 1500 spherical, stainless steel grinding media of 3mm
25 average diameter,
26 150g distilled water,

27 30g aluminium powder of 25µm average particle diameter
28 and

29 2g octyl phosphonic acid

30 was charged to a 500ml pot and milled on a vibratory
31 mill for 1.5 hours.

32 After removing the grinding media, the milled material
33 was screened on a 325 mesh (45µm) screen and recovered
34 as a granule by the method of Example 12 using as
35 carrier a water soluble part hydrolysed polyvinyl
36 acetate resin. The 80% metal content granule provided

1 a very bright, sparkling coating based on Joncrysyl 537,
2 an aqueous acrylic industrial paint resin manufactured
3 by S C Johnson.

4

5 **Example 16**

6

7 Aluminium pigment, made by the process of example 1 as
8 a water carried paste containing 40g of aluminium
9 metal, was mixed with 13.3 g of Beetle BE 370,
10 hexamethoxymethyl melamine from BIP Speciality Resins
11 Ltd. The mixture was formed into granules by extrusion
12 through a 2 mm diameter die, and dried in an oven held
13 at a temperature of 60°C for 16 hours.

14

15 An aqueous printing ink was made by dispersing 5 g of
16 the dried granule in 5 g of distilled water, and then
17 mixing this dispersion with 15 g of Glascol LS2, a
18 colourless water based ink from Allied Colloids. A
19 drawdown on to white paper showed that the product had
20 a bright metallic silver colour.

21

22 **Example 17**

23

24 The procedure of example 16 was repeated with the
25 Beetle BE 370 replaced by RC-294-J427, an acetylenic
26 diol surfactant from Air Products and Chemicals Inc.
27 The dried granular product so formed gave a brilliant
28 metallic silver effect when made up into a Glascol LS2
29 ink.

30

31 **Example 18**

32

33 A dispersion of
34 7.5 g Molywhite 212, a basic calcium zinc molybdate
35 from Sherwin Williams Chemicals
36 1.5g oleic acid

1 2.5g Pluriol P600
2 2.5 g Antarox V27
3 25.0 g distilled water
4 was added to
5 30 g of a fine particle size aluminium powder
6 100 g distilled water
7 1500 g of 1/8 inch diameter stainless steel balls
8 and milled on a vibratory mill for 3.5 hours.
9

10 A flaked aluminium paste product was extracted from the
11 grinding media. If required, the paste can be
12 converted into granular form as described in previous
13 Examples.

1 CLAIMS

2

3 1. A process for preparing a low- or non-dusting,
4 substantially non-volatile metal flake pigment
5 composition, said process comprising ball milling
6 atomised metal powder in the presence of a milling
7 fluid, together with either an additive having
8 both lubricating and corrosion inhibiting
9 properties or with a lubricant and at least one
10 corrosion inhibitor; wherein said milling fluid
11 consists substantially of water.

12

13 2. A process as claimed in claim 1 which includes the
14 step of screening the milled composition to select
15 particles of the desired size.

16

17 3. A process as claimed in either one of claims 1 and
18 2 which includes the step of forming a coherent
19 paste of an organic binder medium, water and metal
20 flake pigment.

21

22 4. A process as claimed in claim 3 wherein said paste
23 is formed by mixing a first component comprising
24 organic binder medium and a second component
25 comprising metal pigment, with either or both of
26 the first and second components comprising water
27 and the paste containing from 3-70% of the organic
28 binder medium based on the weight of the metal
29 pigment, and either sub-dividing the coherent
30 paste into particles and removing substantially
31 all volatile liquids from the particles, or
32 removing substantially all volatile liquids from
33 the coherent paste and sub-dividing the resulting
34 mass into particles, at least 98% by weight of the
35 resulting particles being retained on a sieve
36 having a 150 μm aperture and each containing a

1 plurality of metal pigment particles dispersed in
2 a matrix of organic binder medium, the organic
3 binder medium being capable of binding the metal
4 flake pigment particles by either precipitation
5 from solution during volatile liquid removal, or
6 sintering or melting at elevated temperature and
7 fusion.

8

9 5. A process as claimed in any one of claims 1 to 4
10 wherein said lubricant comprises an ethylene oxide
11 condensate with alcohols or phenols, and a fatty
12 acid or a derivative thereof.

13

14 6. A process as claimed in any one of claims 1 to 5
15 wherein said corrosion inhibitor is a phosphorus-,
16 chromium-, vanadium- or silicon-containing
17 compound.

18

19 7. A process as claimed in claim 6 wherein said
20 corrosion inhibitor is a phosphate ester having a
21 polyethylene oxide side chain.

22

23 8. A process as claimed in any one of claims 1 to 4
24 wherein a single moiety acts as lubricant and
25 corrosion inhibitor.

26

27 9. A process as claimed in claim 8 wherein said
28 moiety is a phosphate ester having a polyethylene
29 oxide side chain.

30

31 10. A process as claimed in any one of claims 1 to 9
32 wherein a surfactant is present in said milling
33 step.

34

35 11. A process as claimed in any one of claims 1 to 10
36 wherein the metal pigment is of aluminium, zinc,

- 1 copper, tin, nickel, iron or alloys thereof.
- 2
- 3 12. A process as claimed in any one of claims 1 to 11
4 wherein the metal pigment is of aluminium or gold
5 bronze.
- 6
- 7 13. A process as claimed in any one of Claims 1 to 12
8 wherein the metal pigment is a highly light
9 reflective pigment.
- 10
- 11 14. A process as claimed in any one of claims 1 to 13
12 wherein the metal pigment is aluminium, the
13 lubricant is oleic acid and the corrosion
14 inhibitor is a phosphate ester having a
15 polyethylene oxide side chain.
- 16
- 17 15. A process as claimed in any one of claims 1 to 14
18 which includes a step of treating the milled metal
19 pigment flakes in an aqueous system.
- 20
- 21 16. A process as claimed in claim 15 wherein said
22 milled metal pigment flakes are treated with
23 chromate, coated with silica or coated with
24 alumina.
- 25
- 26 17. A process as claimed in any one of claims 1 to 15
27 wherein said pigments are coated with micronised
28 binder and sintered.
- 29
- 30 18. Use of a phosphate ester having a polyethylene
31 oxide side chain as an additive in a process of
32 ball milling a metal powder.
- 33
- 34 19. A paste comprising a ball-milled metal flake
35 pigment, water and agent(s) having lubricating and
36 corrosion inhibiting properties.

- 1 20. A paste as claimed in claim 19 comprising ball-
2 milled aluminium or gold bronze flake pigment,
3 water and a phosphate ester having a polyethylene
4 oxide side chain.
- 5
- 6 21. A granule containing a plurality of milled metal
7 pigment particles dispersed in a matrix of organic
8 binder medium without any organic solvent present.
- 9
- 10 22. A granule as claimed in claim 21 which is a
11 sintered granule and wherein said metal pigment
12 particles are dispersed in a matrix of micronised
13 organic binder medium.
- 14

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02912

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09C1/62 C09C1/64 C09D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C09C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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X	GB 1 191 204 A (SHOWA ALUMINUM POWDER CO.) 13 May 1970 see example 5 & US 3 565 655 A (...) cited in the application ---	1,5, 10-13,19
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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1

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INTERNATIONAL SEARCH REPORT

International Application No

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